NASA TT F-10,099

CHEMICAL REACTIONS ON THE SURFACES OF GLASS FIBERS USED IN GLASS-REINFORCED PLASTICS

Ye.B.Trostyanskaya, A.M.Poymanov, and A.V.Skorova

Translation of "Khimicheskiye reaktsii na poverkhnosti steklyannykh volokon, primenyayemykh dlya izgotovleniya stekloplastikov". Plasticheskiye Massy, No.11, pp.67-69, 1965.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON APRIL 1966

CHEMICAL REACTIONS ON THE SURFACES OF GLASS FIBERS USED IN GLASS-REINFORCED PLASTICS

*/67

Ye.B.Trostyanskaya, A.M.Poymanov, and A.V.Skorova

24917

The chemical reactions of functional groups on the surface of glass fiber, used as reinforcement for plastics, are reviewed and their interaction with the filler molecules is described. Readily separated ions on the glass-fiber surface were replaced by trivalent and tetravalent ions, rendering the fiber hydrophobic and eliminating the retarding action of the hydroxyl ions on the setting of the polycondensation-type binders. This resulted in a tougher plastic with a more resistant surface. Author

The functional groups on the surface of glass fibers determine their interaction with the binder, and consequently also the properties of glass-reinforced plastic itself. To improve the characteristics of glass-reinforced plastics, the functional groups on the surface of the glass are modified either by treating the fiber with acid (replacing the alkali-metal ions by protons) or by adding epoxy groups. Most often the glass-fiber surface is modified by adding fillers (Bibl.1 - 3).

As a rule, this is accomplished with organosilicon compounds or organochromium complexes, which react with the hydroxyl groups on the glass surface. This forms a new surface on the glass fiber, with new functional groups able to interact with the binder (Bibl.4 - 6).

---

* Numbers in the margin indicate pagination in the original foreign text.

The molecules of the filler react not only with the functional groups of the fiber, but also with each other, until a protective film is formed. This complicates determination of the relationship between the properties of the glass-reinforced plastic and the type of functional groups chemically attached to the surface of the glass fiber (Bibl.7).

To define this relationship, we modified the glass fibers by the method of heterogeneous-phase ion exchange, replacing the readily separated monovalent and divalent ions on the fiber surface by trivalent and tetravalent ions. We also developed a method of direct addition of organic radicals to the glass fiber, which had not been done previously (except for the reaction with epichlorohydrin). Only methods for modification of the surface of silicon oxide and aluminosilicate powders had been known (Bibl.8 - 10). In those studies, for the most part, organic radicals were added by the Grignard reaction over the interaction of organomagnesium compounds with a pre-chlorinated silica surface according to the scheme:

$$\equiv Si{-}OH + SOCl_2 \longrightarrow \equiv SiCl + SO_2 + HCl$$
$$\equiv Si{-}Cl + BrMgR \longrightarrow \equiv Si{-}R + MgBrCl$$

Silanol groups (Bibl.11) are present on the surface of glass fibers (especially after acid treatment); we therefore considered this method suitable for the addition of organic groups to the surface of aluminoborosilicate, silica, and quartz fibers.

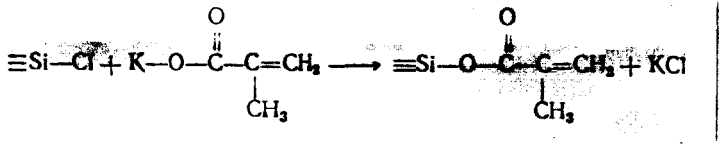
The fibers were first chlorinated by anhydrous thionyl chloride in great excess. After drying for 20 min at 350° C to remove adsorbed moisture, the fibers were treated for 2 hrs in boiling thionyl chloride. The excess of thionyl chloride was washed off the fiber surface by dry carbon tetrachloride until disappearance of thionyl chloride from the wash solvent.

The chlorine added in this manner was determined by removing it with 0.1N KOH and then titrating with 0.1N $AgNO_3$. The chlorine content of the chlorinated aluminoborosilicate fiber was 0.03 - 0.04 mg-equiv/gm.

The chlorinated fiber was treated with organomagnesium reagents in the following manner: A weighed portion of fiber was placed in a three-necked flask provided with a condenser, a dropping funnel, and a stirrer, after which 100 mℓ absolute ether was added. An ethereal solution of allyl (or phenyl or ethyl) magnesium bromide was then added dropwise, and the mixture was boiled for 3 hrs. After cooling, the Grignard reagent was decomposed with water and the fiber was thoroughly washed with water, ethanol, and ether until a pure filtrate was obtained.

The methacrylate groups were added by treating the chlorinated fiber with a 5% solution of the potassium salt of methacrylic acid in ethanol for 30 min at room temperature.

The reaction probably proceeds according to the formula



After treatment, the specimen was washed with distilled water until the filtrate gave a neutral reaction.

A quantitative determination of the organic radicals attached to the fiber surface proved impossible with the methods proposed for siliceous powder materials, since the surface of the glass fibers is much smaller than that of the powders. We therefore judged the addition of the organic groups from the changes in the physical properties of the fibers, primarily from the decrease in their power to adsorb water molecules from the air, leading to a decline in their surface electric conductivity (Bibl.12). The decrease in surface energy

should also be reflected in the wettability of the fiber.

The wettability and surface electrical conductivity of the modified fiber was studied on the elementary fibers by the methods previously developed (Bibl.13). For a comparison of our results with those of other authors, we also investigated fibers treated with trimethylchlorosilane (Table 1).

TABLE 1

SURFACE ELECTRIC CONDUCTIVITY AND WETTABILITY OF MODIFIED GLASS FIBER

Type of Radical Combined with Fiber Surface	Surface Electric Conductivity, ohm^{-1}	Angle of Wetting by		
		Water	Carbon Tetrachloride	Nitromethane
Trimethylsilane	$<10^{-13}$	90°	25°	39° 25°—50°
Allyl	$6.2 \cdot 10^{-13}$	55° 35°—75°	13° 10°—15°	10°
Ethyl	$9.1 \cdot 10^{-13}$	53° 35°—65°	7° 0—15°	7° 5°—10°
Phenyl	$1.7 \cdot 10^{-13}$	50° 30°—60°	0°	20° 15°—25°
Methacrylate	$2 \cdot 10^{-13}$	40° 35°—50°	0°	10°
Untreated fiber	$1.6 \cdot 10^{-11}$	0°	0°	0°

It will be seen from Table 1 that there exists a relation between the wettability of the fiber (especially by water) and its surface conductivity. The sharp decline in the wettability of the fibers with modified surface, and the decrease in their surface electric conductivity, indicate that the organic radicals are chemically combined with the fiber.

The quantity of allyl and ethyl radicals so combined is entirely sufficient to make the fiber as hydrophobic as fillers of the AM-2 and MR-1 types /68 (Bibl.14), which form a continuous polysiloxane film on the fiber surface.

The lower hydrophobic properties imparted to the fiber by phenyl or methacrylate groups may perhaps be due to the fact that their polarity is higher than that of allyl or ethyl and their concentration on the fiber surface is lower.

Glass fiber treated with trimethylchlorosilane is most hydrophobic of all, since it has three methyl groups for each hydroxyl group substituted on the surface.

Analogous results were obtained on the modified silica and quartz fibers (Table 2).

A comparison of the wettability of glass, silica, and quartz fibers by water reveals considerable differences in their surface properties. This is confirmed by the difference in surface electric conductivity in an atmosphere at relative humidity of 95% (1.6×10^{-11} ohm^{-1} for glass fiber, 3.3×10^{-12} ohm^{-1} for silica fiber, and 2.5×10^{-13} ohm^{-1} for quartz fiber). After addition of the organic radicals, the surface properties of the fibers of all three types become the same. Obviously, the surface of fibers modified by the proposed method loses its specific features, and its new properties are determined by the nature of the radicals added.

Current recommendations are that modified fibers filled with conventional compositions be used as soon as possible in the manufacture of glass-reinforced plastics, since they deteriorate markedly during storage. The experience in storage of modified fibers has shown only slight impairment of their hydrophobic properties after two months in air at 20° C and relative humidity of 60%.

The wettability of glass fiber after storage in air for two months is characterized by the following data:

Type of Radicals Added to Fiber Surface	Angle of Wetting by Water
Trimethylsilane	80°
Allyl	45°
Ethyl	40°
Phenyl	30°
Methacryl	35°

We have shown elsewhere (Bibl.15) that on hydrating glass fibers with an elevated content of monovalent and divalent ions, their surface is enriched in free hydroxyl ions, which retards the hardening of the polycondensation resins (phenol formaldehyde, organosilicon, etc.) in the layers in contact with the glass fiber surface. This phenomenon weakens the adhesion of resin to fiber and causes internal stress concentrations at the points of contact.

TABLE 2

WETTABILITY OF SILICA AND QUARTZ FIBERS WITH MODIFIED SURFACE

Group Added to Fiber Surface	Angle of Wettability of Silica Fiber by			Angle of Wettability of Quartz Fiber by		
	Water	Carbon Tetrachloride	Nitromethane	Water	Carbon Tetrachloride	Nitromethane
Trimethylsilane . . .	90°	15° 10°—20°	48° 40°—57°	67° 55°—80°	16° 10°—22°	34° 30°—45°
Allyl . . .	55° 50°—65°	12° 5°—17°	27° 20°—36°	57° 47°—65°	9° 6°—15°	31° 25°—40°
Ethyl . . .	46° 30°—57°	9° 5°—15°	24° 20°—35°	52° 45°—65°	10° 5°—15°	29° 25°—35°
Phenyl . . .	40° 40°—60°	8° 5°—15°	24° 20°—35°	50° 40°—55°	7° 5°—12°	27° 25°—35°
Methacrylate . . .	30° 25°—37°	5° 0°—12°	17° 15°—27°	35° 27°—47°	5° 0°—10°	21° 15°—27°
Untreated fiber . . .	27° 23°—32°	0°	18° 10°—25°	29° 20°—45°	0°	17° 10°—27°

To confirm this opinion as to the cause of the poorer quality of plastics reinforced with glass fibers that contain monovalent and divalent ions, and to eliminate this shortcoming, we modified the fiber surface by substituting difficultly separated ions (titanium, aluminum, chromium) for the readily separated

ions.

The replacement of mobile ions by polyvalent ions seems more rational to /69 us than their replacement by hydrogen ions, accomplished by the conventional treatment of glass fiber with acid solutions. In the latter case, a gel of silicic acid is formed on the fiber surface. This gel readily adsorbs moisture, which retards the hardening of the binder and impairs the strength and dielectric properties of the glass-reinforced plastics.

The mono- and divalent ions were substituted by placing the fiber in an excess of an aqueous solution of titanium tetrachloride, aluminum trichloride, or chromium trichloride. Ion-exchange equilibrium was established in 24 hrs after which the glass fiber was washed with water to neutral reaction, and then dried in air. With decreasing number of readily separated ions on the fiber surface after the ion exchange, the surface conductivity also decreased:

Substituent ion:	H^{+}	Cr^{+++}	Al^{+++}	Ti^{++++}	Untreated Fiber
Surface conductivity at rel. hum. 95%, ohm^{-1}	3.3×10^{-12}	3.1×10^{-12}	2.1×10^{-12}	1.2×10^{-12}	1.6×10^{-11}

The greatest change in the properties of the fiber surface was obtained by substitution of titanium ions for the monovalent and divalent ions.

We used fiber with aluminum and titanium ions, to prepare press molding compositions of organosilicon resin.

The interaction of binders of various types with glass fibers modified by organic radicals, as shown elsewhere by us (Bibl.14), differs only slightly from their interaction with filled fibers. This was confirmed by a comparison of the strength of glass-reinforced plastics prepared from fibers of both types.

The modification of glass fiber by substitution of ions on their surface was accomplished for the first time, so that it was of interest to make a stress

analysis of plastics reinforced by these fibers. It could be assumed that the substitution of readily separated ions by less mobile ones on the fiber surface would decrease the number of hydroxyl ions. This would favorably affect the hardening of polycondensation binders during the manufacture of glass-reinforced plastics and the strength of such products, especially at elevated temperatures.

Fibers with aluminum and titanium ions were used to prepare press molding compositions based on organosilicon resin, which were then subjected to strength tests at 20 and 450° C (Table 3).

TABLE 3

STRENGTH OF ORGANOSILICON GLASS FILAMENTS PREPARED FROM MODIFIED-SURFACE FIBER

Treatment of Glass Fiber	Bending Strength, kg/cm²	
	at 20 °C	at 450 °C
Without plasticizer. . .	925 755—1180	34 14—80
Treated with $AlCl_3$ . . .	1112 1000—1255	217 150—430
Treated with $TiCl_4$ . . .	1220 1050—1350	230 150—300

As shown in Table 3, the substitution of monovalent and divalent ions of the glass fiber surface by trivalent and tetravalent ions does in fact improve the strength of press molding compositions, especially at elevated temperatures.

Conclusions

1. We determined the conditions for modifying the surface of glass, silica, and quartz fibers by combining them chemically with organic radicals to form a new surface whose properties are determined by the nature of the radical.

2. The substitution of readily separated ions on the glass fiber surface by trivalent and tetravalent ions renders the fibers hydrophobic and eliminates the retarding action of the surface hydroxyl ions on the hardening of polycondensation-type binders, which improve the quality of glass-reinforced plastics.

BIBLIOGRAPHY

1. Kiselev, B.A.: Glass-Reinforced Plastics (Stekloplastiki). Goskhimizdat, 1961.
2. Hagen, H.: Glass-Fiber-Reinforced Plastics (Glasfaserverstärkte Kunststoffe). Berlin, 1961.
3. - Glass-Reinforced Plastics. Morgan, ed. (Stekloplastiki, pod red. Morgana). Izd. Inostr. Lit., 1960.
4. Renner, U.: Silikat Tech., No.12, 1961.
5. Matting, A. and Haferkamp, H.: Glastech. Ber., No.1, 1964.
6. Hinz, W. and Solaw, G.: Silikat Tech., No.5, 1957.
7. - Mod. Plastics, No.12, 1962.
8. Shcherbakova, K.D. and Slovetskaya, K.I.: Dokl. Akad. Nauk SSSR, Vol.111, No.4, 1956.
9. Neymark, I.Ye., Sheynfayn, R.Yu., and Svintsova, L.G.: Dokl. Akad. Nauk SSSR, Vol.108, No.5, 1956.
10. Neymark, I.Ye., Chuyko, A.A., and Slinyakova, I.B.: Vysokomolekul. Soyedin. No.5, 1961.
11. Jates, P.C. and Trebilcock, I.W.: SPE (Soc. Plastics Engrs.) Trans., No.4, 1961.
12. Aslanova, M.S.: Doctoral Dissertation, 1954.

13. Trostyanskaya, Ye.B., Poymanov, A.M., and Kazanskiy, Yu.N.: Plasticheskiye Massy, No.7, 1964.

14. Trostyanskaya, Ye.B., Poymanov, A.M., and Kazanskiy, Yu.N.: Plasticheskiye Massy, No.8, 1964.

15. Trostyanskaya, Ye.B., Poymanov, A.M., and Kazanskiy, Yu.N.: Plasticheskiye Massy, No.12, 1964.